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DIFFUSION AND EQUILIBRIUM SWELLING OF

MACROMOLECULAR NETWORKS BY THEIR LINEAR HOMOLOGS

by

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Polydimethylsiloxane (PDMS) networks having strands of molecular weight in the range 11,000-36,000 have been prepared by endlinking linear PDMS molecules of these molecular weights with a tetrafunctional linking agent. Absorption of a series of homologous linear PDMS molecules by the resulting PDMS networks has been investigated. The diffusion coefficients at $70^{\circ}$ were found to be rather large, $1 \times 10^{-12} - 6 \times 10^{-12} m^2/s$, and approximately inversely proportional to the molecular weight of

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20 the diffusing liquid, over the range 5,000-38,000. The amount of liquid absorbed at equilibrium was relatively small, 10% - 80%, in good agreement in all cases with an especially simple version of the Flory-Huggins theory when the heat of mixing is made vanishingly small and only entropic terms are retained.

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## 1. Introduction

Little work has been published on the absorption kinetics and equilibrium uptake of polymeric liquids by polymeric hosts. There are several difficulties in carrying out such experiments and in interpreting the results. Most polymer pairs are incompatible, so that the uptake of one polymer by another is extremely small. Also the diffusion of polymeric liquids is generally slow and the diffusion coefficient is itself a function of concentration when the diffusing liquid has a different segmental mobility from the host material. Nevertheless, the results of such experiments should provide a stringent test of the theories both of molecular dynamics (diffusion) and of thermodynamics of mixtures (equilibrium swelling).

A particularly simple system for experiments of this kind is provided by linear macromolecules having reactive endgroups. When the endgroups are linked by tri- or tetra-functional linking agents, a macromolecular network is created. Absorption of further amounts of the linear macromolecules of which this network is composed takes place at a rate dependent upon the diffusion coefficient and to a final extent dependent upon the thermodynamics of mixing.

Certain experimental and theoretical difficulties are absent in this simple system. Because the swelling liquid and the host material are virtually identical, little change

is expected in the effective segmental mobility as the concentration of the diffusant increases. Also, because of the virtual identity of the two components the heat of mixing is expected to be close to zero. Significant amounts of absorption should therefore be obtained even though the swelling liquids are polymers. Indeed, the thermodynamics of swelling equilibrium take a particularly simple form when the heat of mixing is zero. The experimental results should then provide a powerful measure of the entropic contributions to the free energy of swelling for molecular networks in contact with compatible fluids. Moreover, by varying the molecular length of the swelling macromolecules with respect to the length of the molecules comprising the network, the effect of molecular weight upon the diffusion coefficient and upon the equilibrium uptake can be studied.

Difficulties in reaching swelling equilibrium in reasonable times were minimized in the present experiments by employing polydimethylsiloxane fluids and networks for which the glass transition temperature is extremely low, $-120^{\circ}C$. Measurements were carried out at an elevated temperature, $+70^{\circ}C$, i.e., about $200^{\circ}C$ above the glass transition temperature, so that the effective segmental mobility was relatively high. The results are presented in the following sections of the paper and compared with the predictions of simple theoretical formulations for the dif-

fusion kinetics and degree of swelling at equilibrium of polymeric networks imbibing linear homologs.

## 2. Experimental details

### a. Preparation of polydimethylsiloxane networks

Linear polydimethylsiloxanes having vinyl endgroups were obtained from Dow Corning Corporation. Three different molecular weight ranges were employed for preparing networks. Vapor phase and membrane osmometry yielded values for $\overline{M}_n$ of 10,000, 24,000, and 37,000 g/g-mole. Endgroup analysis using mercuric acetate (1) gave vinyl contents of 0.47 ± 0.03, 0.24 ± 0.02, and 0.15 ± 0.02 percent, corresponding to values for $\overline{M}_n$ of 11,500, 22,500, and 36,000 g/g-mole. GPC data gave $\overline{M}_w/\overline{M}_n$ ratios of approximately 2.0, as reported by Valles and Macosko (2,3) for their similar polymers.

A tetrafunctional silane linking agent, tetrakisdimethylsiloxysilane, was supplied by Prof. Macosko. Gas chromatography, carried out by Prof. Macosko, revealed that it was approximately 89 percent pure. Si-H group analysis (1) gave an average functionality of 3.50, somewhat different from the expected value of 4, indicating that other constituents are present.

The linking agent was mixed with the divinyl polymer, together with about 5 ppm of a Pt catalyst (4). The mixture was then degassed and cast as a thin sheet on a Teflon surface. Measurements were made of the degree of swelling by

benzene after periods of heating at 70°C. As the
endlinking process continued, the degree of swelling of the
resulting gel decreased. Complete reaction was found to
occur after heating for about 3 days at 70°C, as judged by
the equilibrium swelling measurements. Test sheets were
therefore prepared by heating for 4 days at 70°C to ensure
complete reaction.

Networks were prepared in all cases using the amount of
endlinking agent necessary to give a minimum degree of swel-
ling by benzene. This amount was 30 - 50 percent greater
than the calculated stoichiometric quantity, even after allo-
wance had been made for the reduced functionality of the
linking agent. Thus, the junction points were clearly not
exclusively tetrafunctional in nature.

b. Characterization of polydimethylsiloxane liquids

Six polydimethylsiloxane liquids were employed as
swelling liquids including the three liquids from which
networks had been prepared by endlinking. All of the
liquids were characterized by end-group titration, yielding
values for $\overline{M_n}$ between 4,700 and 38,900, Table 1. Viscos-
ities were determined at 23°C and 70°C by a falling-ball
technique using the relation (5)

$$\eta = 2(\rho_s - \rho_\ell) g \, a^2/9v$$

where $\underline{\eta}$ is the liquid viscosity, $\rho_s$ and $\rho_\ell$ are the densities
of the ball and liquid, 7,800 and 970 kg/m$^3$, respectively,

$g$ is the acceleration due to gravity, $a$ is the ball radius (0.794 mm) and $v$ is the terminal velocity of fall, which ranged from about 0.1 to 10 mm/s. The values obtained for $\eta$ are given in Table 1 and are plotted in Figure 1 against the number-average molecular weight $\overline{M}_n$, using logarithmic scales for both axes. The results are seen to be consistent with two linear relations in this representation, having slopes of unity at low molecular weights and 3.5 at high molecular weights. This dependence of viscosity upon molecular weight is commonly observed for polymeric fluids (6), and the critical molecular weight $M_b$ at which the transition takes place from one slope to the other has been generally taken as a measure of the molecular length between entanglements in high-molecular-weight liquids. In the present instance $M_b$ is approximately 17,000, Figure 1. When allowance is made for the use of number-average values for molecular weight in the present experiments, this result is in reasonably good agreement with other determinations of $M_b$ for polydimethylsiloxane liquids, ranging from 24,000 to 37,000 (7,8).

The direct proportionality between viscosity and molecular weight at low molecular weights is consistent with the theoretical relationship of Debye and Bueche (9,10)

$$\eta = \rho_\ell A (\overline{R^2}/M) n\, f/36$$

where $A$ is Avogadro's number, $\overline{R^2}$ is the mean square

distance between the ends of a randomly-coiled macromolecule and $\underline{M}$ is its molecular weight, $\underline{n}$ is the number of monomer units per molecule and $\underline{f}$ is the frictional resistance to motion per monomer unit. When a value of 5.3 x $10^{-21}$ $m^2$/g-mole is assigned to the characteristic ratio $\overline{R^2}/\underline{M}$ (11) the results given in Figure 1 yield values for $\underline{f}$ of 3.0 x $10^{-11}$ N s/m at 23°C and 1.5 x $10^{-11}$ N s/m at 70°C.

    c.  Measurement of diffusion coefficient $\underline{D}$ and

        equilibrium swelling ratio $\underline{Q}$.

Test specimens of each network were cut from cast sheets in the form of thin plates, about 25 mm square and about 1.5 mm thick. They were immersed in the various liquid polymers at temperatures of 23°C and 70°C. Measurements were made of the weight uptake $\underline{m_t}$ at intervals of time until an equilibrium value $\underline{m_\infty}$ was reached. This took several weeks in some instances. In order to ensure that no interlinking with the imbibed polymer or further endlinking of the test sheets took place during long periods of swelling, some sheets were subsequently extracted with benzene, reweighed, and reswollen, in order to verify that all of the imbibed polymeric liquid could be removed and that the process could be accurately repeated.

    Representative plots of the weight uptake $\underline{m_t}$, relative to the equilibrium value $\underline{m_\infty}$, are shown in

Figures 2 and 3, plotted against $t^{\frac{1}{2}}$, where $t$ is the time of immersion of the sample in the swelling liquid. Values of diffusion coefficient $D$ were calculated from the initial linear portions of the experimental relations, i.e., employing the relation for the early stages of diffusion

$$m_t/m_\infty = 4(Dt/\pi \ell^2)^{\frac{1}{2}} \tag{1}$$

where $\ell$ is the thickness of the sample (12). The full curves in Figures 2 and 3 were then calculated from the theoretical relations for the entire diffusion process (13):

$$m_t/m_\infty = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[-D(2n+1)^2\pi^2 t/\ell^2\right] \tag{2}$$

assuming a concentration-independent diffusion coefficient.

Although agreement with the theoretical diffusion equations was found to be excellent in the early stages of diffusion, for weight gains of up to about one-half of the final amount, the experimental results diverged thereafter from the theoretical relations, being more protracted than theory predicts. This slowing down in diffusion in the later stages is tentatively ascribed to thickening of the sample, i.e., an increase in $\ell$, as a result of the swelling process itself. An alternate explanation in terms of selective absorption initially of lower molecular weight components of the swelling liquid was shown not to hold. The swelling liquid was extracted from a partially-swollen sample and found by endgroup analysis to have the same value

of number-average molecular weight $\overline{M_n}$ as the liquid in
which the sample was immersed. Thus, no significant amount
of selective absorption appeared to take place in the
present experiments.

The volume swelling ratio $Q$ was obtained directly
from the equilibrium weight gain $m_\infty$, relative to the initial
weight $m$ of the sample:

$$Q = 1 + (m_\infty/m).$$

3.  **Experimental results and discussion**

a.  Diffusion

Values of the diffusion coefficient $D$ were determined
for each combination of polymeric fluid and polymer network,
from the initial slopes of plots like those shown in Figures
2 and 3.  They are given in Table 2.  They are seen to be
relatively large, reflecting the low frictional resistance
$f$ to segmental motion for PDMS liquids at a temperature
some $200^\circ C$ above their glass transition temperature.  The
values of $D$ are also seen to fall within a relatively
narrow range, considering the rather large range of average
molecular weight of the diffusing liquids and of the network
strands of the elastomeric solids into which they diffuse.
This dependence upon molecular weight is now explored in
some detail.

When the molecular weight of the diffusing liquid is
equal to that of the network strands of the solid into which

diffuses, then the process closely resembles self-

fusion. The coefficient $\underline{D}$ may then be regarded as a

sure of the coefficient $\underline{D'}$ of self-diffusion. Values

$\underline{D'}$ were obtained either directly from measurements with

olymeric liquid diffusing into a network prepared from

same material by endlinking, or indirectly, by extrapo-

ing the measured diffusion coefficients $\underline{D}$ over a range

network strand lengths to obtain the value when the

and molecular weight was the same as the molecular weight

the diffusant. Values obtained in this way are given in

le 1, and plotted against average molecular weight $\overline{M}_n$ in

ure 4, using logarithmic scales for both axes. In this

resentation the results fall on a straight line with a

pe of -1, within experimental error, indicating an

erse proportionality between the coefficient of self-

fusion and molecular weight over the entire range of

ecular weights employed: 4,700 - 39,000.

Comparison between viscosity $\underline{\eta}$ and coefficient $\underline{D'}$ of
self-diffusion.

According to Bueche (10,14), the product $\underline{D'\eta}$ should be

ependent of molecular weight and temperature (except for

irect proportionality to absolute temperature) and given

$$D'\eta = (\rho A/36) (\overline{R^2}/M) kT. \tag{3}$$

Employing appropriate values for the terms on the right hand side of equation 3, the product $\underline{D'\eta}$ is predicted to be about $4.1 \times 10^{-13}$N at $70^\circ$C. This value is in reasonably good agreement with that obtained from experimental values of $\underline{D'}$ (Figure 4) and $\underline{\eta}$ at low molecular weights (Figure 1),

$$\underline{D'\eta} = 6.3 \times 10^{-13}N.$$

An alternative way of making this comparison is to calculate the segmental friction coefficient $\underline{f_o}$ from the measured diffusion coefficients using the theoretical relation (15)

$$D' = kT/f_o N.$$

The magnitude of $\underline{f_o}$ obtained in this way is about $9.5 \times 10^{-12}$Ns/M, in good agreement with that obtained from viscosity measurements, about $1.45 \times 10^{-11}$Ns/m. These values are also in good agreement with an upper limit of $9 \times 10^{-12}$Ns/m obtained for linear PDMS liquids at $30^\circ$C by Barlow, Harrison, and Lamb using viscoelastic relaxation measurements (16).

Thus, the measured coefficients of self-diffusion for PDMS materials, determined as described earlier, are in good agreement with independent measurements of viscosity. Both measures suggest that molecular motion in PDMS liquids and networks is largely unrestrained by molecular entanglements up to number-average molecular weights of about 17,000 for $\underline{\eta}$ and up to at least twice this value for $\underline{D'}$.

It is particularly noteworthy that the diffusion coefficient $\underline{D'}$ does not appear to depend more strongly on molecular weight at the higher molecular weights. Theoretical considerations of tunnel motion (reptation) suggest that $\underline{D'}$

should be proportional to $\underline{M}^{-2}$ ( 17  ).  Bueche suggested a proportionality to $\underline{M}^{-3.5}$ for entangled molecules ( 14 ). Apparently, tunnel-like restraints or entanglements do not affect self-diffusion over the present range of molecular weights.

c.    Diffusion in networks.

Diffusion into a molecular network of PDMS is strongly affected by the molecular weight of the diffusing liquid, as would be expected.  Results given in Table 2 show that the diffusion coefficient for a given network increases by a factor of 3 to 4 as the molecular weight of the diffusant is decreased by a factor of about 8.

The molecular weight of the strands comprising the network appears to have a similar, but somewhat smaller, effect. For  a given diffusant, the diffusion coefficient increases by 40 - 70 per cent as the strand molecular weight is decreased by a factor of about 3.  It is somewhat surprising that tighter networks should allow more rapid diffusion of a given diffusant, in the same way (but to a lesser degree) as a host liquid of decreasing molecular length.  Apparently, the more rapid motion of shorter network strands outweighs  the restrictive effects of network topology on diffusion past them of a polymeric liquid.

d. Equilibrium swelling

Values of the equilibrium volume swelling ratio $Q$, calculated
from the weight of PDMS liquid taken up at equilibrium,are given
in Table 3 for each combination of PDMS network and PDMS swelling
liquid. The amount of swelling liquid taken up ranged from 10-20
per cent for the highest molecular weight liquid up to 50-80 per
cent for the lowest molecular weight liquid. These values are
now compared with the predictions of the Flory-Huggins swelling
theory (18 ), which takes the form:

$$Q^2 \ln(1-Q^{-1}) + Q + \chi + (M_s/M_c)(Q^{5/3}-2Q/f) = 0 \qquad 4.$$

when the densities of the swelling liquid and the polymer network
are assumed equal. In this relation, $M_s$ denotes the molecular
weight of the swelling liquid, $M_c$ is the network strand molecular
weight, $f$ is the functionality of the junction points where the
network strands are interconnected and $\chi$ is a parameter describing
the (unfavorable) heat of interaction between the network polymer
and the swelling liquid.

For the present systems, it is certainly true that the
densities of the swelling liquid and the polymer network are
effectively equal. The functionality $f$ of the endlinking agent
was, in principle, 4, but in practice it appeared to be about 3.5
by titration of SiH groups ( 1). This difference does not greatly
affect the predictions of equation 4 and a value of 3.5 has been
employed hereafter.

The principal unknown quantities in equation 4 are the inter-
action parameter $\chi$ and the network strand molecular weight $M_c$. The
former might well be assumed to be zero for a swelling liquid that

is virtually identical to the network strands with which it comes into contact. When $\chi$ is given the value zero, and $M_s$ is equated to $M_c$ then equation 4 predicts that the swelling ratio $Q$ will be 1.442, i.e., the weight gain will be about 44 per cent. This is a surprisingly large value, about twice as large as the values observed experimentally when the molecular weight of the swelling liquid was equal to the molecular weight of the network strands. As the results given in Table 3 show, the experimental values under these circumstances ranged from 21 to 27 per cent.

However, it is rather naive to assume that the appropriate value of $M_c$ in equation 4 is, indeed, given by the molecular weight of the molecules from which the network was made by endlinking. In fact, the term containing $M_c$ reflects the elastic resistance of the network to expansion. A more appropriate value of $M_c$ is therefore obtained from the tensile modulus of elasticity (Young's modulus $E$) using the relation ( 18 )

$$E = 3\rho R\, T/M_c. \qquad\qquad 5$$

When values of $M_c$ were determined for each network in this way, they were found to be considerably smaller than the molecular weights of the precursor molecules, only about one-half as large, due to the additional restraints from molecular entanglements and the $C_2$ term in the strain-energy function. The degree of swelling with liquids having a molecular weight of only about one-half of that of the precursor molecules is considerably larger, about 35-48 per cent, Table 3, and thus it is relatively close to the value predicted by equation 4.

A complete comparison is shown in Figure 5 between the predictions of equation 4 for the degree of swelling at equilibrium and the

measured values for each network swollen by each liquid. Values of $M_c$ for each network were determined from the elastic modulus $\underline{E}$, using equation 5. The agreement between theory and experiment is reasonably good over the entire range. It is interesting to note that the results are relatively insensitive to the value chosen for the interaction parameter $\underline{\chi}$, at least for swelling liquids having molecular weights comparable to or greater than those of the network strands.

4. Conclusions

Diffusion of PDMS liquids into PDMS networks is readily observed, even for relatively high molecular weight liquids. The diffusion coefficients are quite large at $70^{o}C$, 1 to 6 x $10^{-12}m^2/s$, and approximately inversely proportional to the molecular weight of the diffusing liquid over the range 5,000 to 38,000 g/g-mole. For the lower molecular weight liquids the diffusion coefficients are in good agreement with values calculated from the flow viscosity of the same liquids, using Bueche's relation between the coefficient of self-diffusion and viscosity, equation 3. Thus, diffusion into networks appears to resemble self-diffusion, especially when the molecular weights of the network strands and of the diffusing liquid are equal. The only anomalous feature observed was the lack of agreement at high molecular weights, above about 17,000, where the flow viscosity followed a different dependence upon molecular weight, reflecting the presence of molecular entangle-ments, whereas the diffusion coefficient continued to follow an inverse proportionality. It is concluded that the influence of molecular entanglements upon the diffusion of polymeric molecules does not become apparent until a substantially higher molecular weight is reached than in the case of liquid-like flow.

The amount of liquid absorbed at equilibrium was found to range from 10 to 80 per cent, depending upon the molecular weight of the diffusing liquid relative to the network strand molecular weight. When the Flory-Huggins theory of swelling equilibrium for polymer networks is specialized to the case of a swelling liquid having the same density as the network material, and with

zero heat of interaction, then it is found to be in reasonably good agreement with the experimental measurements of the amount of absorbed liquid. Thus, the swelling of polymeric networks by homologous polymeric liquids appears to be in good agreement with a simple version of the thermodynamics of swelling equilibrium. However, it should be noted that the theoretical results are relatively insensitive to the value chosen for the heat of interaction over virtually the entire range of values that characterize swelling liquids. Instead, they are strongly dependent upon, and dominated by, the elastic resistance of the network to isotropic expansion.

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Table 1.  Number-average molecular weight $M_n$, viscosity $\eta$
and coefficient $D'$ of self-diffusion for polydime-
thylsiloxane liquids.

| $M_n$ (g/g-mole) | $\eta$ at 23°C (N s/m²) | $\eta$ at 70°C (N s/m²) | $D' \times 10^{12}$ at 70°C (m²/s) |
|---|---|---|---|
| 4,700 | 0.15 | 0.075 | $6.3 \pm 1.0$[a] |
| 11,500 | 0.46 | 0.20 | $3.5 \pm 0.5$ |
| 22,500 | 2.5 | 1.15 | $1.75 \pm 0.25$[a] |
| 24,900 | 2.6 | 1.20 | $1.25 \pm 0.25$ |
| 36,000 | 9.0 | 4.2 | $1.25 \pm 0.18$ |
| 38,900 | 9.4 | 4.45 | $0.95 \pm 0.2$[a] |

[a] obtained by extrapolation from $D$ vs $\overline{M}_n$ of network.

Table 2.  Diffusion coefficient $\underline{D}$ ($m^2/s \times 10^{12}$), calculated from equation 1, for PDMS liquids diffusing into PDMS networks.

Molecular weight

| $\overline{M_n}$ of diffusant (g/g-mole) | Network strand molecular weight $M_c$ (g/g-mole) | | |
|---|---|---|---|
| | Measurements at 70°C | | |
| | 11,500 | 22,500 | 36,000 |
| 4,700 | 4.91 ± 0.65 | 4.49 ± 0.60 | 3.63 ± 0.49 |
| 11,500 | 3.52 ± 0.48 | 3.74 ± 0.52 | 2.43 ± 0.34 |
| 22,500 | 1.71 ± 0.24 | 1.75 ± 0.25 | 1.33 ± 0.19 |
| 24,900 | 1.58 ± 0.23 | 1.38 ± 0.21 | 1.02 ± 0.15 |
| 36,000 | 1.89 ± 0.27 | 1.67 ± 0.24 | 1.26 ± 0.18 |
| 38,900 | 1.72 ± 0.25 | 1.34 ± 0.20 | 0.98 ± 0.15 |
| | Measurements at 23°C | | |
| 4,700 | --- | --- | 1.63 ± 0.23 |
| 11,500 | --- | --- | 0.99 ± 0.15 |

Table 3.  Equilibrium volume swelling ratio $\underline{Q}$ for PDMS
networks swollen by PDMS liquids at $70^{\circ}$C.

Molecular weight

$\overline{M}_n$ of liquid

| (g/g-mole) | Network strand molecular weight $\underline{M}_c$ (g/g-mole) | | |
|---|---|---|---|
| | 11,500 | 22,500 | 36,000 |
| 4,700 | 1.477 | 1.610 | 1.773 |
| 11,500 | 1.271 | 1.375 | 1.572 |
| 22,500 | 1.149 | 1.220 | 1.283 |
| 24,900 | 1.151 | 1.219 | 1.287 |
| 36,000 | 1.109 | 1.162 | 1.211 |
| 38,900 | 1.111 | 1.165 | 1.213 |

## Figure Legends

Figure 1.  Flow viscosity $\underline{\eta}$ of PDMS liquids $\underline{vs}$ number-average
molecular weight $\overline{M}_n$.

Figure 2.  Weight uptake $\underline{m}_t$ of PDMS liquid ($\overline{M}_n$ = 4,700 g/g-mole),
relative to the equilibrium value $\underline{m}_\infty$, $\underline{vs}$ $\underline{t^{\frac{1}{2}}/1}$, where $\underline{t}$
is the time of immersion in the swelling liquid and $\underline{1}$
is the thickness of the sample, a thin sheet of an end-
linked PDMS network having $\underline{M}_c$ = 11,500 g/g-mole.  Full
curve calculated from equation 2.

Figure 3.  Weight uptake $\underline{m}_t$ of PDMS liquid ($\overline{M}_n$ = 11,500 g/g-mole),
relative to the equilibrium value $\underline{m}_\infty$, $\underline{vs}$ $\underline{t^{\frac{1}{2}}/1}$, where $\underline{t}$
is the time of immersion in the swelling liquid and $\underline{1}$ is
the thickness of the sample, a thin sheet of an end-
linked PDMS network having $\underline{M}_c$ = 36,000.  Full curve,
calculated from equation 2.

Figure 4.  Coefficient $\underline{D'}$ of self-diffusion of PDMS liquids $\underline{vs}$
number-average molecular weight $\overline{M}_n$ .  Filled-in circles,
measured directly; open circles, obtained by extrapolation
as described in the text.

Figure 5.  Equilibrium volume swelling ratio $\underline{Q}$ $\underline{vs}$ the ratio $\underline{M_s/M_c}$
of the molecular weight of the swelling liquid to that
of the network strands.  $\underline{M}_c$ was obtained from measurements
of Young's modulus $\underline{E}$, using equation 5.  Full curve,
calculated from equation 4 with $\underline{X = 0}$; broken curve, with
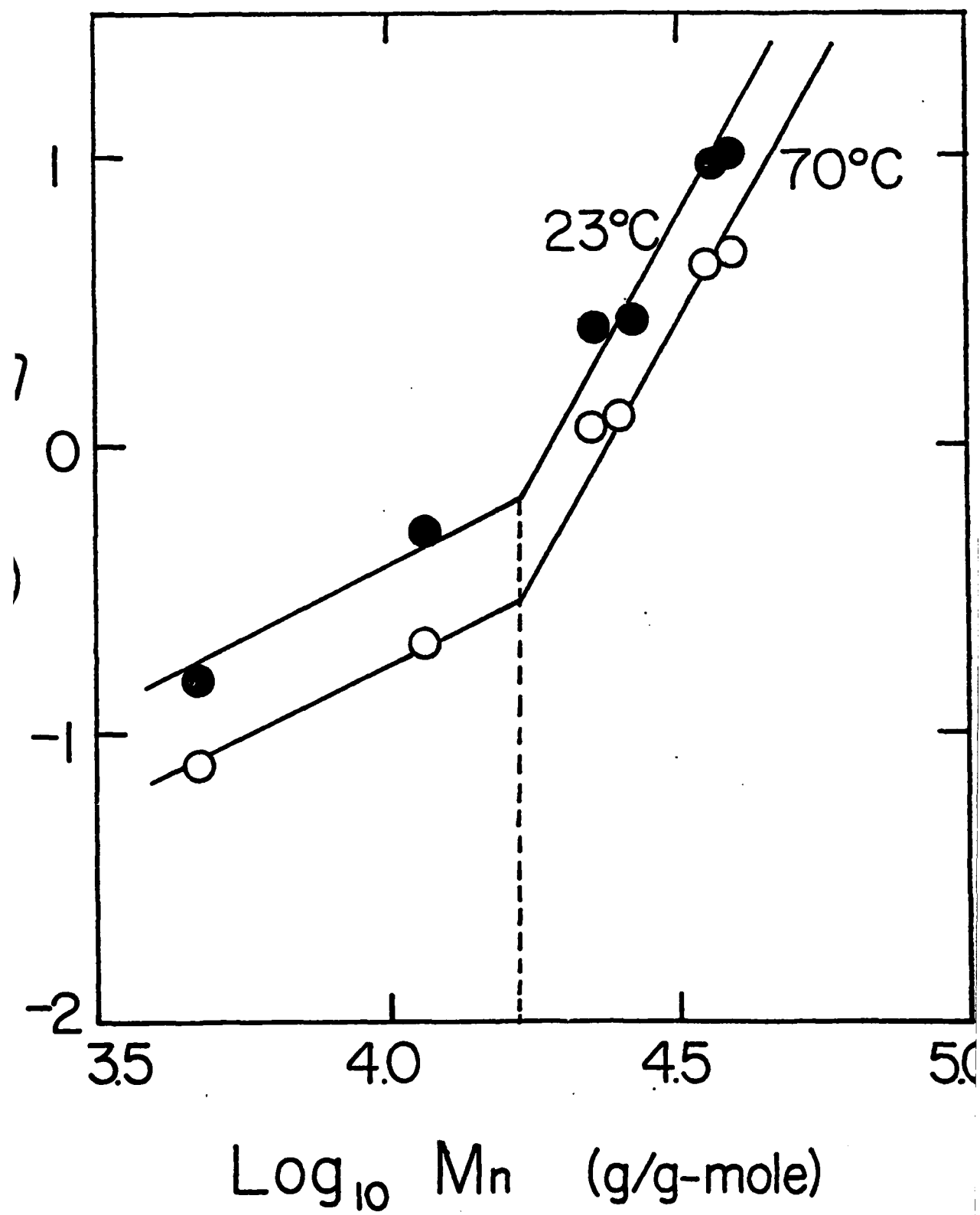$\underline{X = 0.25}$; dotted curve, with $\underline{X = 0.5}$.

FIGURE 1

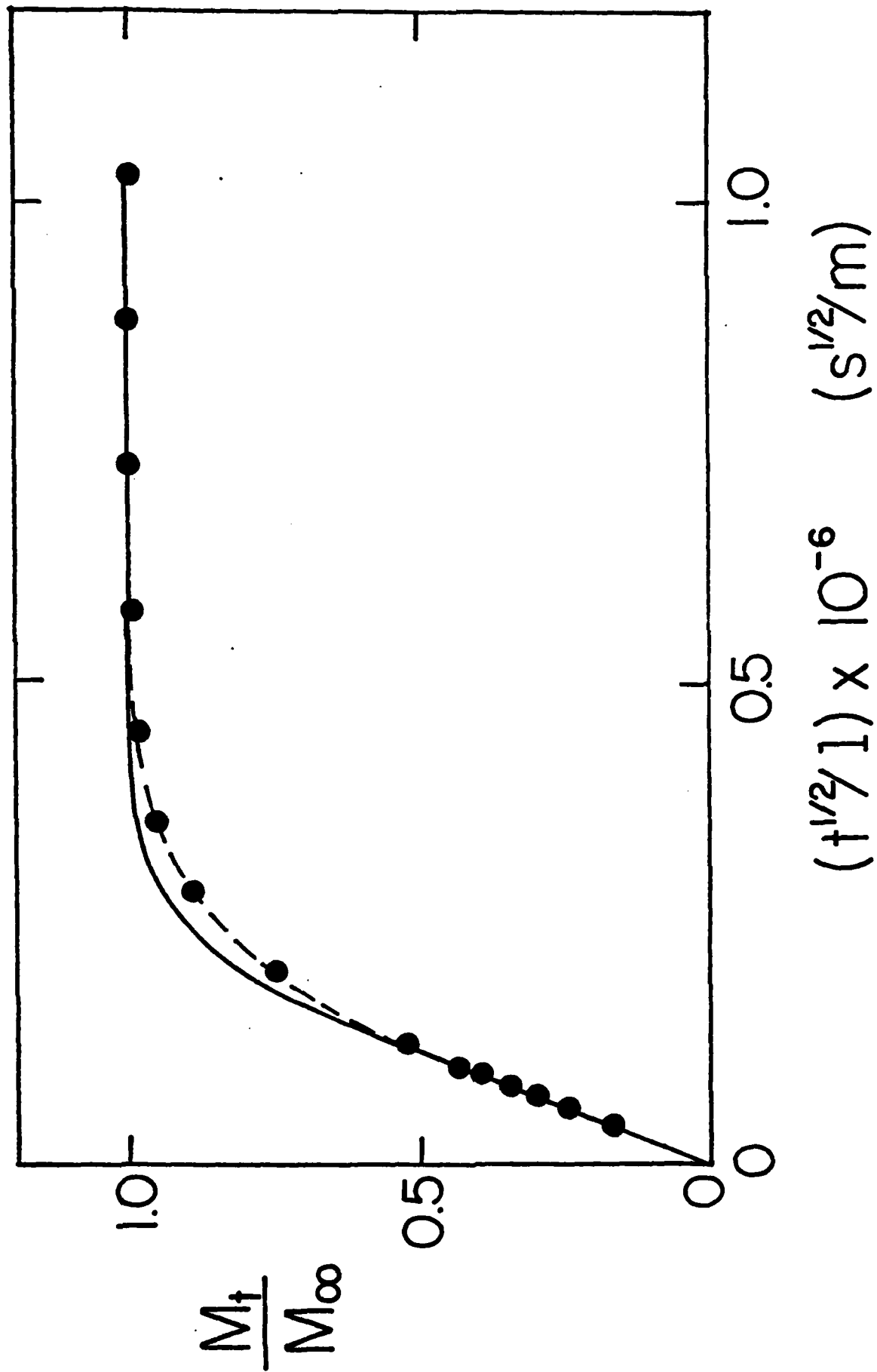FIGURE 2
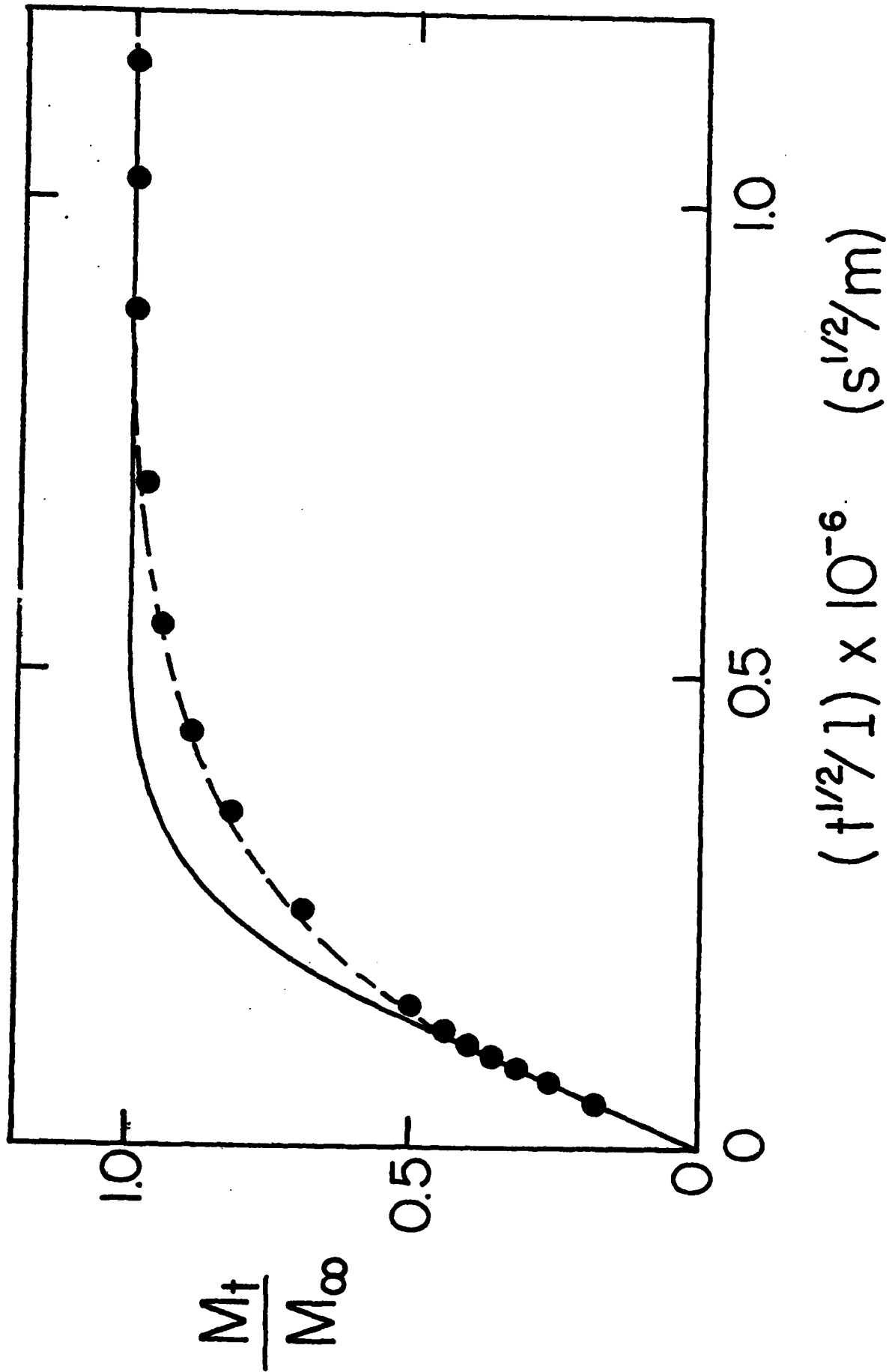
FIGURE 3

FIGURE 4

FIGURE 5

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